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THEORY OF X-RAY DIFFRACTION IN LIQUIDS

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Abstract

There are numerous experimental results in the diffraction of x-rays in liquids that seek explanation by an adequate theory. They may be enumerated at least in part as follows: (1) small scattering intensity near zero diffraction angle, (2) a principal maximum in the intensity-diffraction-angle curve corresponding to distance of molecular separation, (3) the position of this chief maximum as independent of the length of the molecule which forms a straight chain, (4) the variation of the position of a second diffraction peak with carbon content in the case of a normal hydrocrabon or a derivative of a hydrocarbon in a manner that makes the variation of the corresponding "planar" distance (computed by Bragg's Law) with carbon content in the straight chain, a linear one, (5) the similarity of the foregoing variation in solid and liquid saturated normal fatty acids, (6) the agreement of the molecular separation computed by Bragg's Law and other experiments upon the cross-sectional area of straight chain molecules, (7) the alteration in computed separation by attached branches, (8) the presence of three peaks apparently corresponding to three dimensions of a branched chain molecule, (9) the agreement among the computed cross-sectional areas of the three straight carbon chains, normal paraffins, saturated nomal fatty acids and normal alcohols.

The theories of Raman and Ramanathan and of Zernike and Prins give a fairly good account of the first two phenomena just mentioned. But the conception of molecular non-crystalline groupings in the liquid makes possible the use of the crystal powder theory as an idealized one for liquids. It is found that, used as an approximation, this theory explains all the above phenomena.

The Ehrenfest formula, intended by its author for gases but which has been used to obtain the mean molecular separation in liquids, and which varies from Bragg's Law by about 19 percent, cannot be so applied to liquids.

X-RAY diffraction in non-crystalline substances is of increasing interest both from a theoretical and from a practical point of view. The theory of diffraction in liquids presents several difficulties. The molecules are not spherical, the law of force from which the spacial distribution of molecules might be obtained is not known, and probability theorems are not easily applicable to regions which are comparable in dimensions to the distance of separation of the molecule. It is the purpose of the present paper to discuss the present status of the theory of diffraction in liquids, but in so doing the details of current theories will necessarily be omitted.

Theory of Raman and Ramanathan. Perhaps the most complete theory is that of Raman and Ramanathan.[1] The expression they deduce for the intensity of the x-rays of wave-length λ scattered at angles between θ and $\theta+d\theta$ is

$$C_1 \exp\left[-\frac{1}{16}\,\frac{N}{RT\beta}\,\lambda_0^3\left(1-\frac{\lambda_1^3}{\lambda_0^3}\right)^2\right] \qquad (1)$$

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[1] Raman and Ramanathan, Proc. Ind. Assoc. for Cultiv. Science, VIII, II p. 127 (1923).

wherein N is Avagadro's constant, R the gas constant for a gram molecule, β the isothermal compressibility, λ_0 the mean distance between neighboring molecules in the fluid and λ_1 the wave-length of the "structural spectrum" responsible for the scattering of the incident radiation and related thereto by the equation $\lambda = 2\lambda_1 \sin \theta/2$. This expression does give a diffraction-intensity curve that closely resembles those found in liquids. Its exact form seems, however, not so important as other aspects of the contribution of Raman and Ramanathan.

These authors point out that at small angles of scattering there is an analogy with the optical scattering problem. By reference to the work of Lorentz and the use of the statistical thermodynamical theory of light scattering developed by Smoluchowski and Einstein, it is shown that thermal fluctuations of density will produce scattering. Moreover, if the x-ray scattering occurs at a small angle the optical theory can be applied to x-rays. For example in benzene, if $\lambda = 0.71$A, $\theta = 10'$ the thickness of a slab with a path difference of λ would be 239A and hence would contain enough molecules to make the probability considerations apply. Hence the scattering of x-rays would be treated as in optics. But, in magnitude, the scattering from a liquid would be less than from a gas of the same number of molecules. This is because the compressibility is relatively small in a liquid. For benzene the scattering would be one-fortieth of the value in a gas where it is proportional to the number of molecules per unit volume. Thus the reason for the small scattering of x-rays in the region of 0° scattering angle is explained.

By a further discussion the authors of this theory show that, as the angle θ increases, the intensity of scattering increases until $\lambda/(2 \cdot \sin \theta/2)$ is equal to the mean distance of separation of the molecules, at which angle there is a maximum scattering. The explanation of the small intensity near 0° and the presence of a maximum at an angle such that $\lambda = 2\lambda_0 \sin \theta/2$ where λ_0 is the mean molecular distance, is a valuable contribution.

But when Raman and Ramanathan subsequently apply probability considerations developed for a continuum to discrete particles separated by a distance comparable to the volume involved, and thus secure Eq. (1), they probably go beyond what might be called a theory. Eq. (1) is then, in the writer's view, interesting but not acceptable. Nevertheless, Raman and Ramanathan have given the most satisfactory discussion of the problem up to the present time. They have accounted for small scattering near 0° and the presence of a maximum at an angle related to the mean separation of molecules by Bragg's crystal-diffraction law. Variation in density caused by thermal elastic waves explains the interference phenomenon.

Theory of Zernike and Prins. Inasmuch as the law of force between molecules is not known, it would be advisable to express the intensity of scattering as a function of the space distribution of molecules and the angle, and then to ascertain this space distribution by observation of the intensity. This Zernike and Prins[2] have done. The result of their development gives the final equation

$$rg_0(r) = (1/2\pi^2) \int_0^\infty ds \cdot s \cdot i(s) \sin(sr) \tag{2}$$

wherein r is the distance from a given molecule, $g_0(r)$ is a probability distribution function, s is $4\pi \sin(\phi/2)/\lambda$ with ϕ the angle of diffraction and λ the wave-length, and $i(s)$ is defined as follows

$$i(s) = \frac{I(\phi) - NA^2/2}{NA^2/2} \tag{3}$$

In Eq. (3) N is the number of molecules considered, A is the scattering amplitude of each one, $I(\phi)$ is the actual scattering at the angle ϕ. These authors consider the molecules to be distributed along a straight line with a probable variation in their distance of separation, this variation to be the same as the variation of the free path of a gas molecule in terms of the mean free path. Then by treating the scattering as from a unidimensional grating, an expression for the $I(\phi)$ is found. The reasoning is then extended to three dimensions and the above form of Eq. (2) adopted because of our ignorance of $g(r) = g_0(r) + \rho$, or the probability distribution of molecule centers. It is in fact the probability that in an element of volume dv, which is at a distance r from the central point of any given molecule, another molecular center is found. The authors show that for a small angle of scattering or a large wave-length, the scattered intensities from the fluid and the gas (of the same number of molecules) have the ratio of the compressibilities in these two states. This point agrees with the discussion of Raman and Ramanathan. Moreover, in the discussion of the unidimensional grating, Zernike and Prins show that, with the unidimensional grating and the assumed law of separation as stated, the scattering from the molecules at large values of ϕ approximates $NA^2/2$, whereas at small angles it becomes $NA^2l^2/2(l+a)^2$, where l is the mean separation of molecules and a is the molecular diameter. The latter expression is small if l is relatively small. This again accounts for the small scattering at small angles. The curve of intensity of scattering of the one-dimensional grating as a function of ϕ, shows a series of maxima and minima, decreasing in magnitude as ϕ increases.

The theory of Zernike and Prins adds to the earlier work of Raman and Ramanathan chiefly in the form of Eq. (2), which supplies a method of obtaining $g_0(r)$ and finally $g(r)$ from the observed scattering. But the method does not seem practical. It assumes the function to be symmetrical in r, which, in general, will be contrary to fact. For elongated molecules this variation from assumption may and probably would nullify the entire method.

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[2] Zernike and Prins, Zeits. f. Physik, **41** p. 184 (1927).

Ehrenfest formula. In connection with other theories the formula of Ehrenfest[3] will be cited, not because he intended it to be applied to liquids, which he did not, but because it has been so used by several investigators.[4] Consider the scattering by two electrons at a distance a apart. It is shown that the intensity at an angle ϕ, $I(\phi)$ is

$$I(\phi) \propto (1 + \sin 2\pi\rho/2\pi\rho) \quad \text{where} \quad 2\pi\rho \quad \text{is} \quad (4\pi a/\lambda) \sin \phi/2 \tag{4}$$

This function has maximum values for $2\pi\rho = 0.0$, 7.72, 14.07, etc. Hence the first maximum is at $\phi = 0°$. The second is at

$$(4\pi a/\lambda) \sin \phi/2 = 7.72, \quad \text{or,} \quad a = \lambda/2 \times 0.812 \sin \phi/2 \tag{5}$$

Eq. (5) cannot be used to ascertain the distance of separation of two scattering centers in a liquid because the assumptions of the scattering occurring by independent pairs of centers is not met. Indeed, Ehrenfest states clearly that the formula cannot apply to liquids. For a fairly symmetrical molecule there is an agreement between the value of a and the value, 1.33 $(M/d)^{1/3}$ wherein M is the molecular weight, d the density and the expression is the mean distance of the centers of two neighboring spherical molecules in the case of the densest packing. This interpretation of Eq. (5) should not be regarded seriously. That the apparent numerical agreement is not intrinsically noteworthy is seen if one realizes that such an agreement for the *second* diffraction peak is secured only by the omission of the theoretical *first* peak which occurs at 0° diffraction angle, and which is very much *greater* in magnitude. The disagreement is of greater magnitude than the agreement. Thus the Ehrenfest theory is inapplicable because both its assumptions and its predictions are contrary to the facts obtaining in liquids.

Debye's theory of scattering in gases. One of the ways of finding the interferences due to the interaction of the atoms constituting the molecule would be to perform experiments upon gases of different densities. The intermolecular interference could then be elminated and the interference within a molecule ascertained. The possibility in these experiments when aided by theoretical considerations led Debye[5] to discuss scattering in gases, both with single scattering particles and with pairs. The theory is strictly not applicable to liquids and is mentioned here merely because of an interesting point it presents. If the volume occupied by the gas particles is vanishing small in comparison with the free volume, the maximum intensity occurs at 0°. If the volume of the particles now becomes, for example, one half of the total volume of the gas, if $\lambda = 0.71$A, and if the particle diameter is 2.1×10^{-8} cm, then the maximum occurs at 16°. From this view point, the maximum at an angle other than zero may be regarded as caused by the limitation of the approach of scattering centers. To this extent it is

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[3] Ehrenfest, Proc. Akad. Wet. Amsterdam, **27,** 1184 (1915).

[4] Keesom, Physica **2,** 118 (1922); Keesom and de Smedt, Proc. Amsterdam **25,** 118 (1922) and **26,** 112 (1923); Katz, Zeits. f. Physik **45,** 97 (1927).

[5] Debye, Jl. of Mathematics and Physics, **4,** p. 133 (1925) and in German in Phys. Zeits. **28,** 135 (1927)).

in agreement with the thought that the maximum depends upon the mean distance of separation of the molecules.

Theory of cybotaxis. The above theories do not assume any organization of molecules into a space array. The view point of this laboratory[6] is that every liquid contains a myriad of small groupings of molecules produced by forces acting between them, the groups being neither perfect in form nor permanent. The word cybotaxis means literally "space arrangement" and is adopted to designate this condition in a liquid. It is not a new state of matter, but a descriptive term applying to the physical state of a liquid. It is used for the sake of brevity and of emphasis. We have learned to recognize a crystal as being approximately perfect only in fragments. The liquid goes to a much greater extreme. Its semi-perfect small groups do not even retain their identity. Viscosity is that of groups and of unorganized molecular arrays between them and this does not depend directly upon the structure of a single molecule. The theory of diffraction in such a physical structure cannot be exactly that of crystal powders nor of unorganized molecules as in the foregoing theory of Raman and Ramanathan. But the crystal powder theory may be accepted as applicable to an idealized condition which the liquid state only roughly approximates at any instant. In such a theory Bragg's law holds for the maximum peak in the diffraction intensity curve, provided the beam is monochromatic. If it is not monochromatic, then, in general, the peak will be shifted in a direction dependent upon the shape of the frequency-intensity distribution curve. Moreover such a theory shows at once why the scattering is small near 0° and has a prominent peak in the first order according to Bragg's law, why the peak is broad and why higher orders are relatively weak. The first two are accounted for by the existence of the small groups, the third by the limited size of the groups and the fourth partly by the structure factor of the molecules. In regard to the breadth of the peak, preliminary observations in this laboratory show that it is proportional to wave-length as indicated by the powdered crystal theory of Laue,[7] and represented in the application to cubic crystals by,

$$B=\frac{2}{\cos\,(x_h/2)}\left(\frac{\log_e 2}{\pi}\right)^{1/2}\frac{\lambda}{ma}$$

wherein B is the breadth of peak at half-intensity, x_h is the angle of maximum intensity, λ is the wave-length of the radiation and ma is the total extension of the crystal in a direction perpendicular to the reflecting plane. This formula had been earlier used by other writers but without reference to a derivation.

The above shows that the assumption of the cybotactic condition and the adoption of the powdered crystal theory as an approximate one for

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[6] See series of articles by Stewart and Morrow, Morrow, Stewart and Skinner and Stewart in Physical Review for 1927 and 1928.

[7] Laue, Zeits. f. Kristallographie, **46,** 115 (1926).

liquids, satisfies the principle phenomena herein discussed, viz., the small intensity near 0° and a maximum at an angle satisfying Bragg's law for a distance of separation of the molecules. But it goes further. It seems to account for the relative intensities of two peaks through estimates of the structure factor as in the case of the *n*-alcohols,[8] for the practically linear change of angular position of one of the maxima with content of carbon in straight chains while the other maximum remains unchanged, for the similarity of alteration of peaks in solid and liquid normal fatty acids[9] with change in carbon content, for the agreement of interpretation of diffraction measurements with experiments in monomolecular liquid layers, for the agreement of diffraction measurements on isomers[10] with current chemical views, for the comparison of diameters of the carbon chains with normal alcohols[9] saturated normal fatty acids[9] and normal paraffins,[11] and finally for the explanation of the three maxima[11] which apparently correspond to the three dimensions of the straight chain.[12] It should be mentioned that in the above view thermal vibration must appear in the form of elastic waves.

Conclusions. The general conclusion of the discussion is that the assumption of the molecular groupings in the liquid at any instant, or cybotaxis, with the acceptance of the crystal powder theory as an idealized one for the liquid, explains the phenomena found in the most simple manner.

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[8] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

[9] Morrow, Phys. Rev. **31**, 20 (1928).

[10] Stewart and Skinner, Phys. Rev. **31**, 1 (1928).

[11] Stewart, Phys. Rev. **32**, 153 (1928).

[12] The detailed discussion showing that these phenomena are accounted for adequately is omitted here not only because it would require a lengthy presentation of the experimental material but also because the reader who becomes acquainted with the experiments can readily supply this discussion.